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Alternative energy sources from plants of Western Ghats (Tamil Nadu, India)

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Abstract

Twenty-two taxa of Western Ghats plants were screened as potential alternative crops for renewable energy, oil, hydrocarbon and phytochemicals. The highest hydrocarbon yields were observed in *Carissa carandas* (1.7%), and *Jatropha gossypifolia* (1.7%). The highest polyphenol fraction was observed in *Dodonaea viscosa* (17.1%), *Carissa carandas* (7.7%), *Swietenia mahagoni* (6.6%), and *Jatropha glandulifera* (6.2%). The highest oil content was observed in *Aganosma cymosa* (10.3%), *Carissa carandas* (5.8%), and *Argemone mexicana* (5.0%). *Swietenia mahagoni* yielded the highest protein content with 8.1%. The gross heat value of 4175.0 cal/g(17.5 MJ/kg) for *Lochnera rosea* (pink flowered var.), and 4112.0 cal/g for *Dalbergia sissoo* were the highest among the species analysed. NMR spectra of the hydrocarbon fractions of *Alstonia scholaris*, *Carissa carandas*, *Ichnocarpus frutescens*, *Plumeria rubra*, *Thevetia neriifolia* (white flowered var.), *Vallaris solanacea*, *Lochnera rosea* (pink flowered var.), *Euphorbia hirta*, *E. splendens*, *Artocarpus integrifolia* and *Ficus religiosa* revealed the presence of cis-polyisoprene (natural rubber), whereas *Argemone mexicana* showed the presence of trans-polyisoprene (gutta). Several new crop species were identified with potentially useful compounds. The potential exists for growing these alternate crops in areas of underutilized lands, subsequently stimulating industrial and economic growth.

Keywords: Gross heat value; Hydrocarbon; Oil; Polyphenol

1. Introduction

There is a renewed interest in evaluating crop species as alternative sources of non-conventional energy since fossil fuels are quickly being depleted. Solar energy is converted into a wide variety of by-products by green plants that are competitive with

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synthetic petrochemicals, especially plants containing secondary metabolites such as, oil and hydrocarbon, that are attractive alternate energy and chemical sources. Utilization of whole-plant oils as an alternative source of conventional oils and major industrial feedstocks is gaining greater importance throughout the world [1,2]. There are several reports of plant species evaluated for their potential as an alternate source of energy and hydrocarbon [3–14]. However, no systematic study of Indian plant species is available listing their potential as an alternative sources of energy, hydrocarbon, and other

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phytochemicals. Therefore there is a need to screen and identify potential species from the Western Ghats (Courtallum to Srivilliputhur, Reserve Forests). This area typifies a tropical forest area possessing a rich flora with about 1100 species of the possible 2000 species of South India.

2. Material and methods

2.1. Collection of plant materials

Healthy plant samples belonging to same agroclimatic zone were collected randomly from a minimum of 20–25 populations with 15–20 plants per population. Samples consisting of a total fresh weight of 2000–2500 g were bulked into one sample for chemical analyses. Each sample was subsampled twice. Samples were collected between September and December 1994 and 1995. Twenty-two species selected for investigation were collected from the Courtallum and Srivilliputhur areas (Table 1). Samples from lianas, herbs, and shrubs were clipped at ground level, whereas trees and large shrubs were collected by cutting the current year's growth. During collection, plant samples having an accumulation of secondary products, such as latex, gums, oils, and resins were given priority. Any fruits and seeds remaining on the plant were harvested along with leaves. Harvested plant materials were oven dried

Table 1 Botanochemicals of plant species screened from the Western Ghats, Southern India^a

Species	Habit	Crude protein (%)	Oil (%)	Polyphenol (%)	Hydrocarbon (%)	Saponification value (%)
Papaveraceae Argemone mexicana L.	Herb	3.0 ± 0.15	5.0 ± 0.17	3.7 ± 0.06	0.8 ± 0.07	161.0
Meliaceae Swietenia mahagoni L.	Tree	8.1 ± 0.75	1.6 ± 0.53	6.6 ± 0.11	0.9 ± 0.36	170.3
Sapindaceae Dodonaea viscosa L.	Shrub or small tree	7.3 ± 0.2	3.4 ± 0.09	17.1 ± 0.29	0.8 ± 0.22	241.3
Leguminosae Dalbergia sissoo Roxb.	Tree	2.7 ± 0.33	2.0 ± 0.64	1.4 ± 0.23	1.1 ± 0.3	95.0
Cactaceae Opuntia dilleni Haw.	Shrub	1.6 ± 0.5	2.3 ± 0.39	1.7 ± 0.59	1.3 ± 0.52	193.9
Rubiaceae Gardenia gummifera L.f.	Small tree or Shrub	0.8 ± 0.29	1.9 ± 0.13	2.2 ± 0.38	1.2 ± 0.23	150.5
Apocynaceae Aganosma	Climber	1.5	10.3	1.7	1.2	43.0
<i>cymosa</i> G.Don.		±0.17	±0.26	±0.2	±1.1	

Table 1 (continued)

Species	Habit	Crude protein (%)	Oil (%)	Polyphenol (%)	Hydrocarbon (%)	Saponification value (%)
Alstonia scholaris R.Br.	Tree	0.1 ± 0.14	2.0 ± 0.13	1.7 ± 0.35	1.1 ± 0.29	61.2
Carissa carandas L.	Shrub or small tree	2.7 ± 0.13	5.8 ± 0.16	7.7 ± 0.27	1.7 ± 0.18	216.5
Ichnocarpus frutescens R.Br.	Climbing shrub	2.8 ± 0.28	1.3 ± 0.15	2.2 ± 0.18	1.0 ± 0.17	101.2
Plumeria rubra L.	Tree	1.5 ± 0.24	3.0 ± 0.35	2.3 ± 0.19	1.4 ± 0.35	140.0
Thevetia neriifolia (white flow. var.) Juss.	Small tree	4.3 ± 0.28	2.5 ± 0.34	3.9 ± 0.46	1.1 ± 0.3	105.0
Vallaris solanacea Ktze.	Liana	3.5 ± 0.25	2.0 ± 0.12	3.6 ± 0.19	1.3 ± 0.14	78.1
Lochnera rosea (Pink flow. var.) Reichenb.	Shrub	1.3 ± 0.12	3.7 ± 0.13	4.0 ± 0.17	1.3 ± 0.26	21.4
Asclepiadaceae Marsdenia volubilis T.Cooke	Climbing shrub	1.5 ± 0.13	0.8 ± 0.25	1.3 ± 0.24	1.2 ± 0.6	58.0
Euphorbiaceae Euphorbia hirta L.	Herb	1.2 ± 0.24	1.7 ± 0.33	1.1 ± 0.32	1.4 ± 0.11	41.1
E. Splendens Boj.	Shrub	1.0 ± 0.22	3.0 ± 0.1	6.1 ± 0.36	1.3 ± 0.43	77.0
Jatropha glandulifera Roxb.	Shrub	3.0 ± 0.11	1.6 ± 0.09	6.2 ± 0.22	1.0 ± 0.28	105.0
J. gossypifolia L.	Shrub	1.8 ± 0.33	1.8 ± 0.31	2.2 ± 0.27	1.7 ± 0.35	120.3
Moraceae Antiaris toxicaria Leschen.	Tree	1.9 ± 0.27	2.0 ± 0.27	1.6 ± 0.12	1.3 ± 0.4	58.7
Artocarpus integrifolia L.	Tree	1.3 ± 0.18	1.3 ± 0.11	1.5 ± 0.11	1.0 ± 0.48	63.0
Ficus religiosa L.	Tree	2.1 ± 0.12	2.5 ± 0.22	2.3 ± 0.26	1.2 ± 0.12	30.9

 $[^]aValues$ are means of three replications, $\pm SD.$

at 15-30°C then the entire sample was ground in a Wiley mill to pass through a 1 mm screen.

2.2. Extraction of oil, polyphenol and hydrocarbon

Extractables were removed from the subsamples of each species using primarily acetone and then hexane for 48 h in each solvent in a soxhlet apparatus. The acetone extracts were allowed to dry, and then partitioned between hexane and aqueous ethanol (water:ethanol, 1:7) to obtain 'oil' and 'polyphenol', respectively. The partitioned fractions in each solvent were dried, and weighed for yield. The residue was re-extracted for 48 h with hexane to obtain the 'hydrocarbon' fraction. The extract after solvent removal was dried and weighed for yield [4,5].

2.3. Biochemical studies

Plant subsamples were analysed for protein content using the Kjeldahl method [15], while ash and lignin analyses followed Goering and Van Soest [16]. Oil fractions were saponified by conventional procedures [17]. The percentage of carbon, and hydrogen were determined by an elemental analyser.

2.4. Spectroscopy

NMR spectra of the hydrocarbon fractions were obtained using a Bruker AC 300F NMR Spectrometer (300 MHZ) with tetramethylsilane (TMS) as the internal standard and CDCl₃ as the solvent.

2.5. Gross heat value

Gross heat value of each subsample was determined by using a Toshniwal, model cc.0.1, Bomb Calorimeter [18].

2.6. Statistical analysis

Sampling of each species was replicated three times for extractable oil, polyphenol and hydrocarbon, protein, ash, lignin content, and gross heat value. Values in Tables 1 and 2 are the means of three replications with the standard deviation.

3. Results and discussion

3.1. Oil, polyphenol and hydrocarbon

Botanochemicals of the species analysed are presented in Table 1. Argemone mexicana, and Euphorbia hirta are herbs, while all other species are lianas, shrubs or trees that have a fibre utility value and are suitable for annual pollarding. The surveyed species contained a protein content ranging from 0.1% to 8.1%; oil from 0.8% to 10.3%; polyphenol from 1.1% to 17.1%; and hydrocarbon content from 0.8% to 1.7%. Carissa carandas, and Jatropha gossypifolia had the highest concentration of hydrocarbon with 1.7%. Among the taxa analysed, 19 species had 1% or higher yield of hydrocarbons. Twelve taxa analysed yielded 2.0% or higher oil, and 1.0% or more hydrocarbons. Polyphenol fractions were high in Dodonaea viscosa (17.1%), Carissa carandas (7.7%), Swietenia mahagoni (6.6%), Jatropha glandulifera (6.2%), and Euphorbia Splendens (6.1%). The various uses of the polyphenol fraction are for making adhesives, phenolic resins, antioxidants, and other industrial feedstocks [4,19]. Aganosma cymosa had the highest oil content of 10.3%, followed by Carissa carandas with 5.8%, and Argemone mexicana with 5.0%. Of all the taxa evaluated, seven species had oil yields of 3% or higher. A wide variety of chemical intermediates that are known to be major industrial feedstock such as, sterols, long chain alcohols, rosin and fatty acids, waxes, terpenes, and other hydrocarbons could be obtained from the whole plant oil. Whole plant oils possess a range of polar and non-polar lipids that are used in mixtures [19]. Swietenia mahagoni and Dodonaea viscosa yielded the highest crude protein concentrations of 8.1% and 7.3%, respectively. The saponification value of the oil fractions ranged between 21.4 and 241.3 (Table 1). The saponification value gives an indication of the nature of the fatty acids in the fat since the longer the carbon chain, the less acid is liberated per gram of hydrolysed fat [20].

3.2. Gross heat value

The gross heat value of the species analysed showed that they could have potential use as an intermediate

Table 2
Gross heat value of plant species screened and selected fossil fuels

Species	Ash(%)	Lignin(%)	Gross heat value		
			(cal/g(dry)) ^a	(MJ/kg)	
Papaveraceae					
Argemone mexicana	1.7 ± 0.05	27.3 ± 0.15	3145.0 ± 19.2	13.2 ± 0.08	
Meliaceae					
Swietenia mahagoni	3.0 ± 0.01	53.4 ± 0.14	3291.0 ± 29.9	13.8 ± 0.1	
Sapindaceae					
Dodonaea viscosa	2.1 ± 0.07	47.0 ± 0.2	2525.0 ± 11.1	10.57 ± 0.05	
Leguminosae					
Dalbergia sissoo	0.3 ± 0.04	45.2 ± 0.1	4112.0 ± 11.2	17.2 ± 0.05	
Cactaceae					
Opuntia dilleni	16.4 ± 0.05	22.0 ± 0.12	1888.0 ± 45.9	7.9 ± 0.2	
Rubiaceae					
Gardenia gummifera	0.4 ± 0.1	53.0 ± 0.1	3003.0 ± 25.5	12.6 ± 0.1	
Apocynaceae					
Aganosma cymosa	0.5 ± 0.06	20.0 ± 0.15	3539.0 ± 44	14.8 ± 0.2	
Alstonia scholaris	0.8 ± 0.2	47.4 ± 0.2	3110.0 ± 22	13.0 ± 0.09	
Carissa carandas	2.7 ± 0.1	46.0 ± 0.2	3126.1 ± 32.2	13.1 ± 0.1	
Ichnocarpus frutescens	0.3 ± 0.1	47.0 ± 0.2	3379.3 ± 30.3	14.2 ± 0.1	
Plumeria rubra	1.4 ± 0.07	47.0 ± 0.2	3090.0 ± 11.4	12.9 ± 0.05	
Thevetia neriifolia	1.5 ± 0.08	32.2 ± 0.22	3166.4 ± 19.2	13.3 ± 0.08	
(white flow. var.)					
Vallaris solanacea	0.8 ± 0.2	50.0 ± 0.2	3265.0 ± 49.3	13.7 ± 0.2	
Lochnera rosea	0.5 ± 0.06	34.2 ± 0.25	4175.0 ± 27.9	17.5 ± 0.1	
(pink flow. var.)					
Asclepiadaceae					
Marsdenia volubilis	0.2 ± 0.2	42.0 ± 0.2	3429.2 ± 20.7	14.4 ± 0.09	
Euphorbiaceae					
Euphorbia hirta	0.1 ± 0.1	38.1 ± 0.3	3769.0 ± 20.4	15.8 ± 0.09	
E. splendens	2.9 ± 0.1	56.2 ± 0.3	3684.0 ± 29.1	15.4 ± 0.1	
Jatropha glandulifera	0.9 ± 0.1	48.0 ± 0.3	3608.0 ± 25.9	15.1 ± 0.1	
J. gossypifolia	0.7 ± 0.1	35.0 ± 0.3	3045.1 ± 29.6	12.7 ± 0.1	
Moraceae					
Antiaris toxicaria	6.3 ± 0.02	45.0 ± 0.2	3654.1 ± 17.7	15.3 ± 0.1	
Artocarpus integrifolia	1.8 ± 0.05	45.0 ± 0.3	4089.4 ± 25.8	17.1 ± 0.1	
Ficus religiosa	3.1 ± 0.06	38.1 ± 0.2	3376.2 ± 19.1	14.1 ± 0.1	
Rice straw hulls			$3333.0^{\rm b}$	13.9	
Lignite coal			3888.0 ^b	16.3	
Cattle manure			4111.0 ^b	17.2	

^aValues are means of three replications $\pm SD$.

energy sources. The gross heat value of the taxa were compared to well-known natural fossil fuels (Table 2). The gross heat value of *Lochnera rosea* (pink flowered var.) was 4175.0 cal/g, (17.5 MJ/kg) and *Dalbergia sissoo* with 4112.0 cal/g (17.2 MJ/kg) were higher than that of cattle manure with a gross heat value of

4110.0 cal/g (17.2 MJ/kg). Of the taxa analysed, the gross heat values of 11 species were either higher than that of rice straw hulls (3333.0 cal/g; 13.9 MJ/kg) or lignite coal (3888.0 cal/g; 16.3 MJ/kg). Lignin content varies from 2.0% to 56.2% (Table 2). The ash content ranged from 0.1% to 16.4% (Table 2).

^bRef. [29].

Table 3

Analytical values of carbon and hydrogen fractions of various plant materials

Plant fraction	Carbon (%) ^a	Hydrogen (%) ^a
Whole plant	39.9-50.42	5.3-6.08
Polyphenol fraction	30.1-53.36	4.3-5.6
Oil fraction Hydrocarbon fraction	66.5-80.3 33.6-59.6	6.59-11.6 6.9-9.3

^aSample values are from several different plant species analysed with the range of values given. Analytical values of 10 samples.

Among the taxa analysed, 11 species contained very low ash content (< 1.0%). This would be a positive attribute for the potential fuel candidate, since a high ash content has a negative effect on the gross heat value [21]. Gross heat values of a few species were around 3000.0 cal/g (12.56 MJ/kg) even though their ash content is more than 1.0%. This confirms that such species could be an alternative heat source compared to wood.

3.3. Elemental analysis

Plant species yielding higher amounts of one of the fractions such as protein, oil, polyphenol or hydrocarbon and the extractables were further analysed for carbon and hydrogen fractions. Values for the percentage of carbon and hydrogen for whole plant samples, polyphenol fractions, oil fractions and hydrocarbon fractions are presented in Table 3. Several authors have suggested doing elemental analysis of the hydrocarbon fraction for estimating carbon, hydrogen, nitrogen for comparison with standard hydrocarbons [22–24,31]. The hydrogen to carbon ratio is not only an indicator of the elemental composition, but also the conversion capability of biomaterials that have hydrocarbon or hydrocarbon like compounds for low molecular weight fuels or chemical raw materials [25].

3.4. Spectroscopy

The NMR spectra of hydrocarbon fractions of Alstonia scholaris, Carissa carandas, Ichnocarpus frutescens, Plumeria rubra, Thevetia neriifolia

(white flowered var.), Vallaris solanacea, Lochnera rosea (pink flowered var.), Euphorbia hirta, E. splendens, Artocarpus integrifolia, Ficus religiosa produced peaks at 1.68 and 2.03 ppm matching the peaks produced by cis-polyisoprene (natural rubber) [26]. Cis-polyisoprene is the most common hydrocarbon polymer found in green plants. Low molecular weight rubbers could be used as a rubber plasticizing agents, adhesive additive, hydrocarbon feedstock, and prevulcanized for use in the rubber industry [10,11]. Argemone mexicana contained a trans-polyisoprene (gutta) substance producing a peak at 1.62 ppm [5]. Trans-polyisoprene could have large scale applications as both a thermoplastic and a thermosetting resin [5]. In addition to the peaks at 1.68, 1.62 and 2.03 ppm, a peak at ~ 0.9 ppm was found in the spectra of Swietenia mahagoni, Alstonia scholaris, Carissa carandas, Ichnocarpus frutescens, Plumeria rubra, Thevetia neriifolia (white flowered var.), Vallaris solanacea, Lochnera rosea (pink flowered var.), Marsdenia volubilis, Euphorbia hirta, Artocarpus integrifolia, and Ficus religiosa indicating that the polyisoprene also contained the 3,4 moiety [27].

3.5. Ethnobotanical uses

External application of aqueous boiled bark extract of root and shoot of Ficus religiosa is used to cure boils, itching, and pain. Ground leaf of Euphorbia hirta, if taken internally, stops oozing blood while urinating. Its leaves strengthens the body by providing higher quantities of minerals, and also if taken as curry induces lactation. The mucilaginous fleshy tissue of Opuntia dilleni, if taken internally cures stomach ache caused by excessive heat. The application of its charred fruit on the site of a scorpion sting detoxicates and relieves the bite sensation. The fruit of Carissa carandas pickled with ginger hastens digestion and acts as a mild laxative. The intake of an aqueous boiled root extract cleans the uterus after child birth. Latex of Argemone mexicana when applied to the eye will cure cataracts, and reddening and itching of the eyes. Moreover, intake of an aqueous mixture of leaves and seed extract is reported to cure coughs and tuberculosis [28].

4. Conclusions

Preliminary investigations indicated that several species are capable of yielding acceptable amounts of oil, polyphenols, and hydrocarbons. Bio-induction studies on these plants are warranted to increase the quantity of extractables as was achieved by Jayabalan et al. [29]. All parts of the plants can be used for diverse purposes. This study indicates that several species should be considered as potential sources of fuel oil, energy, and hydrocarbon. Tree crops are more economical compared to other crops, as they need to be established only once. Tree crops need minimal quantity of water, fertilizer and pesticide [30]. Collection of phytochemical data on woody Indian plants will make their data readily available for identifying promising species for future consideration for plantations in unused, marginal, and waste lands.

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